

UNITED STATES PATENT APPLICATION

OF

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FOR

SEMI-INSULATING GaN AND METHOD OF MAKING THE SAME

GOVERNMENT RIGHTS IN INVENTION

[0001] Work relevant to the subject matter hereof was conducted in the performance of DARPA Contract No. N00014-02-C-0321. The government may have certain rights in the invention hereof.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] This invention relates to semi-insulating GaN, and to methods of making same. The semi-insulating GaN material of the invention is useful, *inter alia*, as a substrate for the manufacture of electronic and/or optoelectronic devices.

Description of the Related Art

[0003] Gallium nitride and related III-V alloys have exhibited great potential for high temperature and high-frequency electronic applications. However, due to a lack of large area native GaN substrates, most GaN devices have been grown on non-native (heteroepitaxial) substrates such as sapphire and silicon carbide. The use of such foreign substrates is problematic due to lattice mismatch and TE (thermal expansion) mismatch between GaN and the substrate material. One consequence of TE mismatch is bowing of the GaN/heteroepitaxial substrate structure, which leads in turn to cracking and difficulty in fabricating devices with small feature sizes.

[0004] Conductive GaN substrates have recently become available (e.g., the conductive GaN substrates that are commercially available from ATMI, Inc., Danbury, CT 06810, USA). Such GaN conductive substrates are advantageously employed in applications where the substrate must be conductive and homoepitaxial in relation to associated device structure of GaN. However, in a number of electronic applications such as high frequency electronic applications, a semi-insulating GaN substrate is highly desirable.

[0005] U.S. Patent 6,273,948 issued to Porowski et al describes a method of fabricating highly resistive GaN bulk crystals, by crystallization from a solution of atomic nitrogen in a molten mixture of gallium and Group II metal such as beryllium or calcium, under high pressure of 0.5-2.0 GPa and high temperature of 1300-1700°C. Resistivity of 1×10^4 to 1×10^8 ohm-centimeter (ohm-cm) was achieved. However, the crystal obtained from the process was about 1 cm in size, whereas most commercial electronic applications require a substrate size of at least about 2 inches (> 5 cm) diameter.

[0006] U.S. Patent 5,686,738 (Moustakas), U.S. Patent 6,544,867 (Webb et al.), U.S. Patent 6,261,931 (Keller et al.), and U.S. Patent Application 2002/0096692 A1 (Nakamura et al.), disclose various methods of making semi-insulating GaN films on a foreign substrate. All of these approaches are susceptible to TE mismatch issues, and the resultant bowing, cracking and small feature fabrication difficulties discussed above, and none of such approaches has yielded a commercially viable large-area single-crystal semi-insulating gallium nitride material.

[0007] There is accordingly a compelling need in the art for large-area semi-insulating GaN substrates.

SUMMARY OF INVENTION

[0009] The present invention generally relates to gallium nitride and methods of making same.

[0010] In one aspect, the invention relates to large-area single crystal semi-insulating gallium nitride.

[0011] In another aspect, the invention relates to a method of forming large area, semi-insulating gallium nitride, comprising growing gallium nitride material by a growth process, and during the growth process, doping the growing gallium nitride with a dopant species that is effective to compensate residual donor species in the gallium nitride, wherein the concentration of the dopant species is sufficient to render the gallium nitride semi-insulating.

[0012] A further aspect of the invention relates to a method of forming large area, semi-insulating gallium nitride, comprising growing gallium nitride material by a growth process in which donor species in the growing gallium nitride are compensated, by introducing into the growing gallium nitride one or more deep acceptor species in a sufficient amount to compensate the donor species and produce semi-insulating GaN material.

[0013] Other aspects, features and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a graph of resistivity as a function of inverse temperature for an iron-doped GaN crystal grown in accordance with Example 2 hereof.

[0015] FIG. 2 is a UV-VIS transmission spectrum for a crystal grown in accordance with Example 4 hereof. The crystal is double side polished, 384 μm thick, iron concentration $1.1 \times 10^{19} \text{ cm}^{-3}$, silicon concentration $1.0 \times 10^{17} \text{ cm}^{-3}$, oxygen concentration $4.7 \times 10^{17} \text{ cm}^{-3}$.

[0016] FIG. 3 is a UV-VIS transmission spectrum for a heavily iron-doped, single side polished, 200 μm thick with iron concentration of $3 \times 10^{19} \text{ cm}^{-3}$ and donor impurities silicon of $7.5 \times 10^{17} \text{ cm}^{-3}$ and oxygen of $4.9 \times 10^{16} \text{ cm}^{-3}$.

[0017] FIG. 4 shows a plot of thermal conductivity vs. inverse temperature for the Fe doped sample of Example 4, having an Fe concentration of 10^{19} cm^{-3} and two unintentionally doped (UID) GaN samples grown under similar conditions without the iron.

[0018] FIG. 5 is a UV-VIS transmission spectrum, wherein % transmission is plotted as a function of wavelength in nanometers (nm), for the GaN film formed in Example 6.

DETAILED DESCRIPTION OF THE INVENTION, AND
PREFERRED EMBODIEMENTS THEREOF

[0019] The disclosures of the following patents and patent applications are hereby incorporated herein by reference, in their respective entireties:

U.S. Patent 5,679,152 issued October 21, 1997 for “Method of Making a Single Crystal Ga*N Article;”

U.S. Patent 6,156,581 issued December 5, 2000 for “GaN-Based Devices Using (Ga, Al, In)N Base Layers;”

U.S. Patent 6,440,823 issued August 27, 2002 for “Low Defect Density (Ga, Al, In)N and HVPE Process for Making Same;”

U.S. Patent 6,447,604 issued September 10, 2002 for “Method for Achieving Improved Epitaxy Quality (Surface Texture and Defect Density) on Free-Standing (Aluminum, Indium, Gallium) Nitride ((Al, In, Ga)N) Substrates for Opto-Electronic and Electronic Devices;”

U.S. Patent 6,488,767 issued December 3, 2002 for “High Surface Quality GaN Wafer and Method of Fabricating Same;”

U.S. Patent 6,533,874 issued March 18, 2003 for “GaN-Based Devices Using Thick (Ga, Al, In)N Base Layers;”

U.S. Patent Application Publication No. 20010008656 published July 19, 2001 for “Bulk Single Crystal Gallium Nitride and Method of Making Same;”

U.S. Patent Application Publication No. 20010055660 published December 27, 2001 for “Bulk Single Crystal Gallium Nitride and Method of Making Same;”

U.S. Patent Application Publication No. 20020028314 published March 7, 2002 for “Bulk Single Crystal Gallium Nitride and Method of Making Same;”

U.S. Patent Application Publication No. 20020068201 published June 6, 2002 for “Free-Standing (Al, In, Ga)N and Parting Method for Forming Same;” and

United States Patent Application No. 09/524,062 filed on March 13, 2000 in the names of Robert P. Vaudo, et al.

[0020] The present invention is based on the use of III-V nitride deposition to form large-area semi-insulating substrates. While illustratively described hereinafter in reference to GaN as the III-V nitride material of particular interest, it will be recognized that the invention is not thus limited, but rather extends to and encompasses other III-V nitride species, e.g., (Ga,Al,In)N materials.

[0021] As used in such context, “(Ga,Al,In)N” refers to metal nitride compositions in which the metal moiety can be one, two or all three of such gallium, aluminum and indium metals in appropriate stoichiometric ratio, e.g., GaN, AlN, InN, GaAlN, GaInN, AlInN, or GaAlInN. The stoichiometric proportions of the metals in multi-metal III-V nitride compounds will be understood to encompass integer as well as non-integer values. For example, it is understood that the term GaAlN refers to $\text{Ga}_x\text{Al}_{1-x}\text{N}$ where $0 \leq x \leq 1$. Accordingly, the disclosure hereinafter directed to a “GaN material” or a “GaN process” will be understood to have broad application to such other III-V nitride compositions and their methods of formation.

[0022] As used herein, the term “large area” in reference to the GaN material means that such material has a diameter of at least 25 millimeters, or in the case of square or rectangular wafers, a diagonal dimension of at least 25mm. The thickness dimension desirably is at least 300 micrometers, e.g., a thickness in a range of from about 300 micrometers to about 5 centimeters or more. These dimensions are in reference to the wafers as formed from the original crystal growth single wafers or from boules by steps including initial crystal growth to form the boule or ingot article, followed by rounding, sizing, slicing, lapping, polishing, etc. as necessary to produce wafers having surfaces suitable for epitaxial growth thereon.

[0023] As used herein, the term “free-standing” in reference to the semi-insulating GaN of the present invention means a three-dimensional body of such semi-insulating GaN material that is not physically affixed to or integral with any substrate, i.e., the semi-insulating GaN is a stand-alone article.

[0024] As used herein, the term “semi-insulating” in reference to the semi-insulating GaN material of the invention means that such material has a resistivity > 100 ohm-centimeters ($\Omega\text{-cm}$) at room temperature ($\sim 25^\circ\text{C}$). In one embodiment, the GaN material of the invention may have a resistivity $> 10^2 \Omega\text{-cm}$ at 200°C . In another embodiment, the semi-insulating GaN material may have a resistivity $> 10^5 \Omega\text{-cm}$ at room temperature. More preferably, the semi-insulating GaN material has a resistivity $> 10^5 \Omega\text{-cm}$ at 200°C , and most preferably the semi-insulating GaN material has a resistivity $> 10^5 \Omega\text{-cm}$ at 300°C . Such values of resistivity are determined by four point probing techniques (van der Pauw contact geometry) as a function of temperature. In instances where the GaN material, e.g., as a free-standing substrate article, has microelectronic circuitry fabricated on and/or within such substrate, the GaN material of the invention has a semi-insulating character in the operating temperature regime of such microelectronic circuitry. The term “within” in such context refers to circuitry in which the substrate forms a part of the device, e.g., wherein the substrate is subjected to an implantation process to form implanted device region(s) in the substrate.

[0025] The GaN process used to grow the semi-insulating GaN of the invention may be of any suitable type. While the invention is described primarily hereinafter in specific reference to hydride vapor phase epitaxy (HVPE), it will be recognized that the invention is not thus limited, and that the semi-insulating GaN of the invention can be formed by other growth methods, including iodine vapor phase growth (IVPG), metalorganic chemical vapor deposition (MOCVD), halide vapor phase epitaxy (HaVPE), mechanical sputter epitaxy (MSE), molecular beam epitaxy (MBE) and nitrogen ion cluster epitaxy (NICE).

[0026] In accordance with the present invention, large area, semi-insulating gallium nitride is produced by a growth process in which donor species in the growing gallium nitride are compensated, by introducing into the growing gallium nitride one or more deep acceptor species in a sufficient amount to compensate the donor species and yield a gallium nitride of semi-insulating character.

[0027] The donor species in the grown gallium nitride may derive from defects in the material that are ionized to produce ionized centers and free conductive band electrons. GaN growth processes invariably produce native defects and incorporate

unintentionally doped impurities in the grown GaN material, producing an n-type conductivity GaN product. The unintentionally doped impurities can for example include residual donor ions deriving from impurities in the reaction chamber in which the GaN is grown, e.g., as present in the walls of a quartz growth chamber. These impurities function to lower the resistivity of the GaN material produced in the growth process. For example, HVPE processes produce GaN material having an electron concentration that is typically near $1 \times 10^{16} \text{ cm}^{-3}$ or greater.

[0028] In accordance with the present invention, large-area, semi-insulating GaN material is produced by intentional doping of deep acceptor species in the gallium nitride material during growth thereof, to compensate the donor species deriving from defects and residual incorporated impurities of the grown material.

[0029] The deep acceptor species can be of any suitable type that is compensatingly effective to produce a GaN material that is semi-insulating in character. The deep acceptor species can include one deep acceptor species or more than one such species. In accordance with a preferred aspect of the invention, the deep acceptor species comprises one or more transition metals.

[0030] The transition metals useful in the invention can be of any suitable type or types, e.g., scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, rutherfordium, dubnium, seaborgium, bohrium, hassium, meitnerium, ununnilium, unununium, and ununbium.

[0031] The deep acceptor dopants employed in the practice of the invention accept electrons having an energy level intermediate the valence band and the conduction band of the GaN, e.g., as generated by unintentionally doped impurities or native defects in the material, thereby making the gallium nitride semiconductor into a semi-insulating material.

[0032] The use of deep acceptor dopants in HVPE formation of gallium nitride is carried out in a preferred embodiment of the invention to achieve growth of semi-insulating gallium nitride at high rate and produce thick, large-area GaN material.

[0033] The energy level of the acceptor species is important in determining the conductivity or resistivity of the GaN material at high temperatures. If the activation energy is too small, trapped donor impurities can become thermally activated at high operating temperatures, with the result that the GaN material is more conductive under such conditions. Activation energy of the deep acceptor species useful in the broad practice of the invention is preferably greater than .35 electron volt (eV), more preferably greater than 0.5 eV and most preferably greater than 0.75 eV.

[0034] In accordance with a preferred aspect of the invention, at least one transition metal selected from the group of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd and Hg is employed as a deep level acceptor for forming large-area semi-insulating gallium nitride. Particularly preferred dopant species include Mn, Fe, Co, Ni, and Cu, with Fe being presently most preferred.

[0035] The present invention contemplates large-area free-standing semi-insulating gallium nitride produced by incorporating one or more deep acceptor species during growth. Gallium nitride substrate material in a preferred aspect of the invention is grown using an HVPE process, in which a transition metal is introduced into the growth environment, e.g., into the HVPE growth chamber (reactor), as hereinafter more fully described. For such purpose, the reactor preferably is configured to minimize unintentional impurities in the growth environment. It is generally preferred to maintain unintentional impurities in the grown GaN at a level less than $5 \times 10^{17} \text{ cm}^{-3}$, more preferably less than $1 \times 10^{17} \text{ cm}^{-3}$, even more preferably less than $5 \times 10^{16} \text{ cm}^{-3}$, and most preferably less than $1 \times 10^{16} \text{ cm}^{-3}$.

[0036] Transition metals can be incorporated into the GaN crystal by using one or more corresponding metal source reagents in the gallium nitride growth process.

[0037] When HVPE is utilized as the gallium nitride growth process, the GaN growth can be carried out by contacting hydrochloric acid (HCl) with metallic gallium. The

metallic gallium can be provided in a reservoir (boat), and the contacting with HCl forms gaseous GaCl, which is carried to the growth zone and reacted with NH₃ to form crystalline GaN, e.g., on a GaN seed crystal or other growth substrate. In accordance with the invention, the deep acceptor species is introduced to the growth zone, so that deep acceptor species is incorporated in the growing GaN crystal in an amount effective to compensate the donor species in the GaN crystal and render it semi-insulating, e.g., as having a resistivity greater than 10⁵ Ω-cm at 25°C and at 300°C.

[0038] HVPE processes for forming semi-insulating GaN can be carried out in any suitable manner, such as by adaptation (by doping the growing GaN crystal with a deep acceptor species) of the HVPE process described in U.S. Patent 6,440,823 issued August 27, 2002 in the names of Robert P. Vaudo, et al. for "Low Defect Density (Al,In,Ga)N and HVPE Process for Making Same," or other HVPE processes that are disclosed in the various patents and patent applications identified and incorporated by reference hereinabove.

[0039] In general, GaN growth process in accordance with the invention are desirably carried out with minimization of the "background" impurities in the GaN material deriving from the growth chamber, raw materials for the GaN manufacturing process, or other components or materials of the process system. The process conditions (e.g., temperature, pressure, concentrations, V/III ratio, etc.), gas purity, and reactor construction (including materials of construction and configuration) should in general be optimized to minimize such background impurity concentrations, so that background carrier concentrations are maintained at suitably low levels, e.g., less than 5 x 10¹⁷ cm⁻³, and more preferably less than 1 x 10¹⁶ cm⁻³, or lower. The background carrier concentration comprises native defects and impurities that contribute to conduction in the material.

[0040] As an illustrative example, the HVPE process can be carried out to grow the GaN material, using NH₃, HCl and Ga as reactants, in which the growth process is carried out at a suitable process conditions, e.g., a temperature in a range of from about 985°C. to about 1010°C., a growth rate of from about 50 to about 150 μm per hour, a pressure of from about 10 to about 800 torr, and a NH₃/HCl ratio of from about 2 to about 40, e.g., about 5, to produce a GaN material of suitable low defect density

character, e.g., having a dislocation defect density that is not in excess of 1×10^7 defects/cm², and more preferably not in excess of 1×10^6 defects/cm².

[0041] In another illustrative example, the growth of GaN can be carried out in a two-stage growth procedure, including (1) a first stage in which the GaN material is grown on a substrate at a temperature in a range of from about 950°C to about 1020°C to form GaN material having a dislocation density of 10^7 defects/cm² or lower, with the GaN material having pits on an upper surface of the material at the conclusion of such first stage of the process, and (2) a second stage in which GaN material is grown on the first stage GaN material, at a temperature in a range of from about 1020°C to about 1250°C for sufficient time to at least partially fill the pits formed on the surface of the GaN material in the first stage of the process.

[0042] The deep acceptor doping is carried out during both stages of the process. Such a two-stage process is beneficial since the second stage processing reduces background carrier concentration, making it easier to produce semi-insulating GaN material.

[0043] Particularly preferred process conditions in the first stage of such two-stage HVPE process include temperature in a range of from 985°C to about 1010°C, growth rate in a range of from about 50 to about 150 μm of GaN per hour, pressure in a range of from about 10 to about 800 torr, and the reactants NH₃ and HCl being in a ratio NH₃/HCl that is in a range of from about 2 to about 40, e.g., from about 2 to about 10.

[0044] The GaN material as a further example can be formed by a vapor phase epitaxy process to form a semi-insulating GaN boule, by growing the GaN material on a native GaN seed crystal, or alternatively on a heteroepitaxial substrate (that is removed in situ or ex situ from the resultant GaN boule), at a growth rate that is above 20 micrometers per hour, and preferably above 50 micrometers per hour, with introduction of the deep acceptor dopant into the growing GaN film at a concentration producing semi-insulating GaN material.

[0045] The boule produced by such process can for example have a diameter greater than 25 millimeters, and a length (thickness of the boule in the growth direction) that is at least 1 centimeter, having a crystal quality that yields a double crystal x-ray rocking

curve full width half maximum value of less than 250 arcseconds, and a top surface defect density of less than 10^4 defects cm^{-2} .

[0046] A wide variety of HVPE and other GaN growth processes can be utilized in the broad practice of the present invention, wherein the transition metal doping of the GaN material is carried out during the growth process, to form semi-insulating GaN. In general, HVPE processes are carried out, with deep acceptor doping, at a high growth rate, e.g., on the order of from about 50 to about 250 micrometers per hour, at growth temperatures of from about 950 to about 1150°C, pressures of from about 25 to about 760 torr, and V/III ratio of from about 2 to about 50, more preferably from about 2 to about 40, and most preferably from about 5 to about 40, to form the semi-insulating GaN at a suitable thickness, e.g., of from about 50 micrometers to about 5 centimeters or more.

[0047] The deep acceptor doping of the GaN material during the growth process can be carried out in any suitable manner, as for example in accordance with the illustrative embodiments described below.

[0048] When HVPE is utilized as the gallium nitride growth process, the deep acceptor dopant can be passed to the growth chamber in a carrier gas, e.g., when the deep acceptor component is of vapor form. If the deep acceptor species is a liquid or solid having sufficient vapor pressure, bubbler or vaporizer arrangements can be employed in which the carrier gas is contacted with and entrains the deep acceptor vapor. Alternatively, the deep acceptor species may be delivered to the growth zone as a component of a source reagent, e.g., a deep acceptor transition metal constituting the metal moiety of an organometal compound, which is in vapor form, or is volatilizable by bubbler, vaporizer or the like, for delivery to the growth chamber.

[0049] The deep acceptor species thus can be in any suitable form in which it can be delivered to the growth chamber. The deep acceptor species may likewise be incorporated in, or reacted with, one or more of the raw materials (e.g., Ga, HCl, GaCl, NH₃) that are introduced to, or produced in, the GaN process system. When the deep acceptor is introduced in a precursor form, e.g., in a metalorganic precursor whose metal moiety is the deep acceptor species, the precursor desirably is (i) sufficiently

volatile to enable good transport to the growth chamber, (ii) readily decomposable to yield the deep acceptor species for incorporation in the growing GaN material, or (iii) alternatively reactive or otherwise transformable to effectively incorporate the deep acceptor species in the growing GaN material, and (iv) of sufficient purity so as not to introduce undesirable impurities into the growing GaN material.

[0050] Precursor flow to the growth chamber can be constant, varied, or switched on and off, depending on desired outcome. In most instances, precursor flow will be maintained constant during the incorporation of the deep acceptor in the growing GaN material.

[0051] In one illustrative embodiment of the invention, a transition metal deep acceptor species is mixed with the gallium source forming a solution of the transition metal in gallium. In this arrangement, the HVPE GaN growth reactor apparatus can be maintained in a conventional process configuration, without modification. The transition metal is loaded with gallium into the gallium reservoir, and the HVPE process then is carried out, with the transition metal being incorporated as a dopant in the GaN product material.

[0052] In some applications, this approach may be less preferred than others described hereinafter, since the other approaches enable the amount of transition metal incorporated in the GaN crystal to be modified during the growth process. Recharging of the gallium and the transition metal are required by this approach, in order to adjust the transition metal concentration, or to maintain the transition metal concentration if the consumption rates (of the gallium and transition metal) differ. The amount of transition metal incorporation may be varied with the process history since there may be a preferential reaction with HCl so that the transition metal concentration in gallium varies with time. The advantage of this approach is the simplicity of the process, which can be carried out in an existing HVPE GaN reactor without any hardware modification.

[0053] In another embodiment, the transition metal dopant is placed in a separate boat inside the reactor or in an external source vessel, and HCl is flowed over the transition metal boat, thereby converting transition metal into gaseous metal chloride that is

carried to the growth zone by the carrier gas. The concentration of the gaseous transition metal chloride can be adjusted by regulating the HCl flow and the boat temperature to achieve a specific metal chloride concentration appropriate to the specific semi-insulating GaN growth process.

[0054] In yet another embodiment, transition metal chloride is placed in a separate boat inside the reactor or in an external source vessel, and carrier gas is used to carry the metal chloride vapor to the growth zone. The concentration of the metal chloride vapor can be controlled by adjusting boat/source vessel temperature and carrier gas flow rate as appropriate to the compensating level of the deep acceptor dopant necessary to form the semi-insulating GaN material. The requisite doping concentration of the deep acceptor species for imparting semi-insulating character to the GaN material is readily determinable by simple empirical variation of dopant concentration in successive runs, followed by the characterization of the material produced in each run, by four point probe determination, to determine the concentration best suited to a specific set of process conditions.

[0055] The same approach can be utilized for empirical determination of appropriate process variables and/or reactor configuration and material(s) of construction, since all of these factors can impact the GaN growth process and the nature and extent of compensation of the donor species present in the GaN material.

[0056] Thus, the vapor-phase epitaxial growth process can utilize metal chloride as a gaseous dopant source material that is introduced to the growth zone. This approach requires the use of a transition metal chloride having sufficiently high vapor pressures, and therefore is limited to transition metals with higher metal chloride vapor pressures such as iron. Suitable transition metals can be identified for such approach by measurement of the vapor pressure of the candidate metal chloride compounds, to determine a transition metal chloride compound appropriate to a given application of the GaN growth process.

[0057] In another variant approach, a volatile metal-organic compound can be used as a deep acceptor source reagent, e.g., for a deep acceptor transition metal. Volatile metal-organic compounds useful for such application include, without limitation,

cyclopentadienyl transition metal compounds, such as Cp₂Fe (bis(cyclopentadienyl)iron, also termed ferrocene), Cp₂Mn, Cp₂Co, Cp₂Ni, Cp₂Cr, deep acceptor metal compounds such as metal carbonyls, metal carbonyl derivatives, metal pentanedionates, metal acetylacetones, and other aliphatic and aromatic deep acceptor metal source compounds of sufficiently vaporizable or volatilizable character for delivery to the growth chamber, using delivery techniques such as flash vaporization, bubbler delivery, sublimation, aerosolization, ultrasonic dispersion, etc.

[0058] For example, compounds such as the illustrative cyclopentadienyl compounds discussed above may be delivered to the growth chamber by bubbler delivery techniques, in which the deep acceptor metal cyclopentadienyl compound is a solid at room temperature (~25°C), and has sufficient vapor pressure for use in a bubbler-based vapor feed arrangement. The metal cyclopentadienyl compound is placed in a bubbler outside the main reactor vessel, and carrier gas is passed through the bubbler to entrain the metal-organic vapor and transport it to the growth zone in the reactor chamber. By such bubbler delivery, the concentration of the metal impurity in the GaN crystal can be controlled by the temperature in the bubbler chamber and the carrier gas flow rate, each of which can be independently varied to achieve a specific incorporation of the metal deriving from the metal cyclopentadienyl compound.

[0059] In other embodiments of the invention, the deep acceptor agent can be of any suitable phase (gas, liquid or solid) as appropriate for processing and subsequent incorporation in the growing GaN film to impart semi-insulating character thereto.

[0060] Semi-insulating GaN substrates can be formed in accordance with the invention in a process in which the semi-insulating GaN material is grown on a sapphire, SiC or other suitable heteroepitaxial substrate, following which the semi-insulating GaN material is separated from the heteroepitaxial substrate by a suitable separation process. Such separation of the semi-insulating GaN material from the heteroepitaxial substrate can for example be carried out by in situ removal of the heteroepitaxial substrate at or in the vicinity of the semi-insulating GaN growth temperature, as described more fully in U.S. Patent 5,679,152 issued October 21, 1997 for "Method of Making a Single Crystal Ga*N Article," the disclosure of which is hereby incorporated herein by reference. As further alternatives, parting or separating the semi-insulating GaN

material from the heteroepitaxial substrate material can be effected using parting layers, thermal fracturing techniques, energy impingement on the GaN/heteroepitaxial substrate interface, or in other suitable manner, as more fully disclosed in various of the patents and patent applications identified and incorporated by reference hereinabove.

[0061] As yet another alternative approach, the semi-insulating GaN material of the invention can be grown on a GaN seed, e.g., formed as more fully disclosed in the various patents and patent applications identified and incorporated by reference hereinabove. Such GaN seed can be semi-insulating in character, or the semi-insulating material can be grown on a conductive seed that is subsequently removed (e.g., by polishing, slicing or other removal technique).

[0062] The semi-insulating bulk GaN material of the invention can be formed by vapor deposition techniques such as HVPE, or in other manner, at any suitable thickness and size characteristics. For example, semi-insulating GaN substrates can be formed at thickness in a range of about 300 micrometers to about 5 centimeters, to yield a single wafer, ingot, boule, or other bulk material body, having appropriate dimensions. For example, HVPE methods of the invention can be carried out to yield semi-insulating GaN boules having a diameter on the order of about 50-100 millimeters, at thicknesses of 1.25 cm and greater.

[0063] The bulk material body of the single crystal semi-insulating GaN, once formed, is processed to yield wafer blanks, e.g., by sawing or other technique. The wafer blanks in turn are subjected to lapping, polishing and planarization operations, as necessary, to produce wafers of suitable thickness for use in forming electronic and/or optoelectronic device structure(s) thereon.

[0064] The gallium nitride material may thus be utilized as a semi-insulating substrate for fabrication of an electronic device thereon and/or therewithin. Such electronic device can for example include devices such as a high electron mobility transistor (HEMT), a monolithic microwave integrated circuit (MMIC), etc. Additionally, the gallium nitride material of the invention may be utilized in connection with a conductive substrate, to facilitate device fabrication of microelectronic devices such as high power rectifiers.

[0065] The finished wafer preferably has a low level of dislocation defects below about 10^6 defects cm^{-2} , as determinable by AFM or optical microscopy techniques following suitable defect decoration. For example, small pits (visible by AFM) are formed around threading dislocations following the chemical mechanical polishing (CMP) or hot phosphoric acid etching of GaN wafers. Such dislocations are “decorated.”

[0066] The semi-insulating GaN of the invention is usefully employed for fabricating a wide variety of GaN devices that are currently grown on heteroepitaxial substrate materials such as sapphire or semi-insulating silicon carbide.

[0067] The present invention thus provides a methodology for forming semi-insulating GaN in which donor species in the gallium nitride material are compensated during the material growth process by acceptor species. The acceptor species may include dopant deep acceptor species such as Mn, Fe, Co, Ni, Cu, Cr, etc. as well as compensating impurities deriving from the raw materials, growth chamber materials of construction, etc., which function to compensate the donor species and yield semi-insulating GaN material as the product of the growth process. It correspondingly is within the scope of the invention to utilize multiple impurities as compensating acceptor species. It is also within the scope of the invention to use impurity-defect complexes to compensate residual donors in the growing GaN material, in producing semi-insulating GaN bulk forms.

[0068] The concentration of the dopant/impurity species that is desirable in the GaN growth process of the invention can be readily determined by measurement of resistivity of the GaN material formed, in samples of GaN that have been formed under otherwise corresponding process conditions, but at differing concentrations of the dopant/impurities, wherein ohmic contacts of suitable material (e.g., InSn alloy contacts) are formed on the respective material samples to enable resistivity testing to be conducted. Elevated temperature measurements may be required to accurately determine the resistivity.

[0069] Secondary ion mass spectroscopy (SIMS) can also be employed to measure and tune the background impurity and dopant concentrations.

[0070] By way of specific example, iron doping may be effected with concentrations of from about 3×10^{16} *Fe* atoms/cm³ to about 7×10^{16} *Fe* atoms/cm³, as determined by SIMS or GDMS measurement techniques known to those skilled in the art, in combination with donor concentration less than 3×10^{16} cm⁻³, to yield semi-insulating GaN having a suitable resistivity value, e.g., $\sim 2 \times 10^9$ ohm-cm.

[0071] The semi-insulating GaN material of the invention has a background carrier concentration that is consistent with the semi-insulating character of the GaN material, and such background carrier concentration is desirably as low as possible. For example, the growth process in the absence of the semi-insulating compensation of the invention may produce a GaN material having a background carrier concentration that is in a range of from about 10^{15} to about 10^{18} cm⁻³.

[0072] Conditions of the growth process can be adjusted as necessary to reduce the background carrier concentration, such as by use of growth times that are sufficiently long to reduce defect density and impurity concentration (e.g., of impurities such as silicon, oxygen, sulfur, carbon, phosphorus, chlorine, etc.) to predetermined or otherwise desired levels, which as mentioned should be as low as possible. Background carrier concentration can also be minimized by appropriate adjustment of process conditions such as III-V ratio, growth temperature, pressure, growth rate, etc. Purification of chemical reagents used in the growth process, or use of ultra-high purity reagents is also advantageous to minimize the background carrier concentration, as is avoidance of growth chamber structural components that can undesirably contribute impurities such as silicon, oxygen, etc.

[0073] Consistent with the foregoing, the deep acceptors that are utilized as compensating species in the practice of the invention, and their precursors (when a precursor reagent is employed) are likewise desirably of a high purity character that avoids the undesired introduction of contaminant impurities into the growing gallium nitride material. Additionally, such deep acceptors and precursors are desirably selected to be well-matched to the specific growth process that is utilized to form the semi-insulating GaN material. For example, organometallic precursors employed as sources for transition metal dopant species are advantageously selected to possess

sufficient volatility for efficient transport in the growth environment, and to decompose cleanly and efficiently to yield the desired dopant species or otherwise to react or transform in such manner as to efficiently incorporate the deep acceptor species, without introducing undesirable impurities into the growing GaN material.

[0074] The features and advantages of the invention are more fully shown by the following illustrative non-limiting examples.

[0075] Example 1: HVPE GaN growth incorporating multiple transition metal elements.

[0076] In this example, the efficiency of incorporating transition metals in GaN crystals was determined in an HVPE process.

[0077] One weight percent of each of Cu, Ni, Co, Fe, Mn, and Cr, was added together with the others of such metals, in the gallium boat of an HVPE GaN growth system. After the HVPE reactor was heated to the growth conditions, gallium nitride crystals were grown under the same growth conditions as used for HVPE growth of gallium nitride without transition metal impurities.

[0078] The growth conditions were: growth temperature = 1030°C, growth pressure = 50 Torr, and growth rate = ~100 µm/hour. The transition metal impurity concentration in the grown GaN crystal was analyzed using glow discharge mass spectrometry (GDMS) by a commercial vendor.

[0079] Table I below shows the concentration of impurities in a GaN crystal grown in this example. The concentration of each of Cr, Mn and Co was below the detection limit of the GDMS. The iron concentration was the highest in the GaN film, followed by copper and nickel. This experiment indicated that a mixture of transition metal impurities in the metallic gallium reservoir allowed reasonable incorporation of iron and copper in the crystal during HVPE GaN growth.

[0080] Table I: Impurity Concentration (parts-per-billion, by weight, based on the weight of the GaN film) Measured by GDMS in a GaN Crystal Grown in Example 1.

Transition Metal	Conc. (ppb)
Cr	<5
Mn	<5
Fe	40
Co	<1
Ni	6.5
Cu	25

[0080] Example 2: Semi-insulating HVPE GaN using low-level iron doping

[0081] In this example, the growth and properties of semi-insulating HVPE GaN crystals were demonstrated by incorporating low concentration iron impurity. 2.8 grams of 99.995% pure iron and 250 grams of 99.99999% gallium were loaded into the gallium boat (reservoir) at room temperature. The reactor was sealed and the reactor temperature was raised to the growth temperature.

[0082] GaN crystals were grown on a sapphire template using the baseline growth conditions. The growth conditions were: growth temperature = 1030°C, growth pressure = 50 Torr, and growth rate = about 100 µm/hour. After four-hour growth, the GaN crystals were removed from the reactor and characterized.

[0083] Table II below shows the impurity concentration in a GaN crystal grown in this example. The impurity concentration was measured with secondary ion mass spectrometry (SIMS) by commercial vendor. The iron concentration was about 4×10^{16} Fe atoms cm⁻³, which was slightly higher than the total donor impurity (silicon, oxygen, and carbon) concentration.

[0084] Table II: Impurity Concentration Measured by SIMS in a GaN Crystal Grown in Example 2

Element	Concentration (cm-3)
Fe	4×10^{16}
C	7×10^{15}
Si	1.5×10^{16}
O	2×10^{16}

[0085] The resistivity of the GaN crystal grown in Example 2 was measured as a function of temperature by the four-point probe method using InSn contacts. The contacts were ohmic once the InSn had melted and the temperature of the GaN was above $\sim 60^{\circ}\text{C}$. Figure 1 shows resistivity data, as a function of inverse sample temperature, for the iron-doped GaN crystal sample grown by the method described above. The resistivity at 250°C was 3×10^5 ohm-cm and the resistivity at room temperature (determined by extrapolation) was 2×10^9 ohm-cm. The activation energy for Fe-doped GaN was 0.51 eV, as shown in Figure 1.

[0086] Example 3: Conductive HVPE GaN using low-level iron doping but with high donor impurities

[0087] In this example, the importance of reducing the background donor impurity concentration was demonstrated. This example used a different HVPE reactor configuration than the reactor that was used in Example 2.

[0088] 5 grams of 99.995% pure iron and 800 grams of 99.99999% gallium were loaded into the gallium boat (reservoir) at room temperature ($\sim 25^{\circ}\text{C}$). The reactor was sealed and the reactor temperature was raised to the growth temperature. GaN crystals were grown on a sapphire template using the baseline growth conditions. The growth conditions were: growth temperature = 1030°C , growth pressure = 400 Torr, and growth rate = about 200 $\mu\text{m}/\text{hour}$. Sacrificial growth was carried out prior to the steady state growth process, to let the reactor settle in a stable condition. At start of the steady state growth process, the amount of gallium in the gallium boat was about 600 grams. The amount of iron in the boat was not determined, although the initial iron concentration was 0.6%wt. After three hours of growth, the GaN crystals were removed from the reactor and characterized.

[0089] The crystal grown in this example was not semi-insulating. Room temperature Hall measurement showed that the carrier concentration was $6.6 \times 10^{16} \text{ cm}^{-3}$ and the carrier mobility was $895 \text{ cm}^2/\text{Vs}$. The resistivity of the crystal was 0.1 ohm-cm . The impurity concentration was measured by secondary ion mass spectrometry (SIMS). The SIMS determination of iron concentration was $1.9 \times 10^{16} \text{ cm}^{-3}$, as shown in Table III below. This iron concentration was lower than the total concentration of silicon and oxygen, which accounted for the conductive character of the GaN grown in this example.

[0090] Table III: Impurity Concentration Measured by SIMS and GDMS in a GaN Crystal Grown in Example 3

Element	SIMS (cm^{-3})
Fe	1.9×10^{16}
Si	5.5×10^{15}
O	2.2×10^{17}

[0091] Example 4: HVPE GaN using high level iron doping

[0092] This example involved two samples, each doped with more Fe than Si or O, but with all such dopants being at high concentration in both samples.

[0093] This example shows that if the background impurity level is too high, then it is not possible to simply add more deep acceptor to compensate. There is, instead, a background impurity limit (BIL), which we have determined (for iron; the BIL may depend on the specific compensating species employed) to be about $5.0 \times 10^{17} \text{ cm}^{-3}$, above which concentration the background impurities become non-compensatable by further addition of deep acceptor species to the growing GaN material. For this reason, the GaN background impurities concentration (BIC) should not exceed about $5.0 \times 10^{17} \text{ cm}^{-3}$. In preferred practice, the BIC is less than $1.0 \times 10^{17} \text{ cm}^{-3}$, more preferably being less than $5.0 \times 10^{16} \text{ cm}^{-3}$ and most preferably being less than $1 \times 10^{16} \text{ cm}^{-3}$.

[0094] In this example, 5 grams of 99.995% pure iron and 800 grams of 99.99999% gallium were loaded into the gallium boat (reservoir) at room temperature. The reactor was sealed and the reactor temperature was raised to the growth temperature. GaN crystals were grown on a sapphire template using the baseline growth conditions. The growth conditions were: growth temperature = 1030°C, growth pressure = 400 Torr, and growth rate = about 200 $\mu\text{m}/\text{hour}$. A short sacrificial growth was performed prior to steady-state growth conditions being established, to let the reactor settle into a stable condition. At the start of steady-state growth, the amount of gallium in the gallium boat was about 750 grams and amount of iron in the boat was about 0.6%wt. After three hours of growth, the GaN crystals were removed from the reactor and characterized.

[0095] The impurity concentration was measured by secondary ion mass spectrometry (SIMS) by a commercial vendor. Table IV shows the impurity concentration for the crystal grown in this example.

[0096] The concentration of iron in the crystal was about $1.1 \times 10^{19} \text{ cm}^{-3}$, much higher than the concentration of silicon ($1.0 \times 10^{17} \text{ cm}^{-3}$) and the concentration of oxygen ($4.7 \times 10^{17} \text{ cm}^{-3}$) combined. However, room temperature Hall measurement showed that the crystal was not semi-insulating. The room temperature resistivity for the crystal was 16 ohm-cm, the carrier concentration was $5 \times 10^{15} \text{ cm}^{-3}$ and the carrier mobility was 68 cm^2/Vs . This suggested that iron at high concentration did not completely compensate the donor impurity.

[0097] Table IV: Impurity Concentration Measured by SIMS in the GaN Crystal Grown in Example 4

Element	SIMS (cm^{-3})
Fe	1.1×10^{19}
Si	1.0×10^{17}
O	4.7×10^{17}

[0098] FIG. 2 shows the UV-VIS transmission spectrum for a crystal grown in this example. The crystal was double side polished, 384 μm thick, with an iron concentration of $1.1 \times 10^{19} \text{ cm}^{-3}$, a silicon concentration of $1.0 \times 10^{17} \text{ cm}^{-3}$ and an oxygen concentration $4.7 \times 10^{17} \text{ cm}^{-3}$.

[0099] FIG. 3 shows the UV-VIS spectrum for another crystal (single side polished, 200 microns thickness) that was grown with higher iron concentration in the gallium boat, producing a heavily iron-doped crystal with iron concentration of $3 \times 10^{19} \text{ cm}^{-3}$. The donor impurities were silicon, at a concentration of $7.5 \times 10^{17} \text{ cm}^{-3}$, and oxygen, at a concentration of $4.9 \times 10^{16} \text{ cm}^{-3}$. The crystal was conductive with resistivity of 0.012 ohm-cm, carrier concentration of $1.2 \times 10^{19} \text{ cm}^{-3}$ and mobility of 35 cm^2/Vs .

[00100] Both crystals exhibited n-type conduction. The UV-VIS spectra show a relatively sharp absorption peak at 456.7 nm (2.71 eV), which was attributed to the intracenter transition of Fe^{3+} impurity in the 6A1(s) ground state to the 4E(G) excited state. The broad band absorption at the wavelength below 450 nm was attributed to excitation of the Fe^{3+} 6A1(S) ground state to bounded electron-hole pair (Fe^{3+}). This broad absorption leveled off at about 390 nm (3.18 eV), indicating that the energy level of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ charge transfer was about 3.18 eV above the valence band. The origin of n-type conduction in the heavily iron-doped HVPE GaN crystal was not rigorously determinable, but may have been related to the generation of crystal defects attributable to the high iron concentration. Nonetheless, this example shows that the achievement of semi-insulating GaN is not simply a matter of loading the film with high amounts of the deep acceptor dopant species when background impurities are high in concentration. Instead, as discussed hereinabove, the BIC of the GaN film must be below the BIL for such material, in order for the background impurities to be compensatable to yield a semi-insulating GaN material.

[00101] The dislocation density of the GaN:Fe wafer was measured by counting the etch pit density with an atomic force microscope (AFM) after chemical mechanical polishing (CMP). The chemical mechanical polish decorates dislocations with a slightly different polishing rate in the vicinity of the dislocation. The dislocation density of the GaN:Fe sample with an Fe concentration of 10^{19} cm^{-3} was approximately

$8 \times 10^6 \text{ cm}^{-2}$, similar to that measured for samples grown under the same growth conditions, but with iron absent.

[00102] The thermal conductivity of the GaN:Fe wafer was measured by the laser flash method at different sample temperatures. Figure 4 shows a plot of thermal conductivity vs. inverse temperature for the Fe doped sample with an Fe concentration of 10^{19} cm^{-3} and two unintentionally doped (UID) GaN samples grown under similar conditions without the iron. The thermal conductivity of the first GaN:Fe sample with an Fe concentration of 10^{19} cm^{-3} was 210 W/mK at room temperature ($\sim 25^\circ\text{C}$), similar to that measured for samples grown under the same growth conditions, but with iron absent. The thermal conductivity of several foreign templates is given in Table IV.A below for comparison. The thermal conductivity is much larger than that of sapphire templates typically used during heteroepitaxy.

[00103] Table IV.A

UID: Unintentionally doped GaN: comparison of thermal conductivity of other GaN substrates	
Sapphire	30 W/mK
SiC	300-380 W/mK
Si	140 W/mK
HVPE	220 W/mK

[00104] Example 5: Transition metal doped HVPE GaN using volatile metal-organic as dopant source. This example shows the incorporation of a deep acceptor species in a growing GaN film from a metalorganic precursor, via bubbler delivery.

[00105] This example demonstrated the incorporation of a transition metal in the GaN crystal material, using a metal compound of bis(cyclopentadienyl) as the metal precursor, supplied from a bubbler outside of the reactor. Ferrocene ((bis(cyclopentadienyl)iron), Cp_2Fe) was the specific precursor compound used in this example.

[00106] The gas stream from the bubbler was mixed with ammonia inside the reactor. 250 grams of 99.99999% gallium were loaded into the gallium boat (reservoir) at room temperature (~25°C). The reactor was sealed and the reactor temperature was raised to the growth temperature. GaN crystals were grown on a sapphire template using the baseline growth conditions. The growth conditions were: growth temperature = 1030°C, growth pressure = 50 Torr, and growth rate = about 100 $\mu\text{m}/\text{hour}$. Nitrogen carrier gas was flowed through the ferrocene bubbler and the bubbler was maintained at a temperature of 43°C. The flow rate of the bubbler carrier gas was 200 sccm.

[00107] After one-hour growth on a sapphire substrate, the GaN crystals were removed from the reactor and characterized. Iron and other impurity concentrations in the GaN crystal were analyzed by SIMS technique.

[00108] Table V shows the impurity concentrations that were measured by SIMS. The carbon impurity in the crystal was at the detection limit of the SIMS device, suggesting that the metal-organic precursor did not introduce a significant amount of carbon impurity to the crystal during the growth process. The high oxygen concentration in the crystal was due to a leak into the reactor during this growth. Subsequent growth with better leak-tightness of the reactor resulted in a substantially reduced oxygen impurity level.

[00109] Table V: Impurity Concentration Measured by SIMS and GDMS in the GaN Crystal Grown in Example 5

Element	SIMS (cm^{-3})
Fe	2.1×10^{18}
Si	2.8×10^{16}
O	5.4×10^{18}
C	8.3×10^{16}

[00110] Example 6: Transition metal doping with a separate dopant boat inside the reactor.

[00111] This example demonstrated the incorporation of a transition metal in a GaN crystal, using a separate metal boat inside the growth reactor. In addition to the gallium boat, the reactor was arranged to contain a separate boat for transition metal doping.

[00112] 800 grams of 99.99999% gallium were loaded into the gallium boat, and 5 grams of 99.995% pure iron wire were loaded into the dopant boat. A baseline growth condition was first established without dopant flow. The baseline growth conditions were: The baseline growth conditions were: growth temperature = 1040°C, growth pressure = atmospheric pressure, growth rate = 125 $\mu\text{m}/\text{hr}$.

[00113] In a subsequent growth process, the HCl flow for the dopant boat was turned on, while other conditions were identical to the baseline growth condition. HCl reacted with metallic iron, forming iron chloride that was carried to the growth zone. The HCl flow for the dopant boat was 5 sccm and HCl flow for the gallium boat was 50 sccm. A sapphire substrate was used and the GaN film thickness obtained was 60 μm .

[00114] The presence of iron in the film was evident by UV-VIS transmission spectrum shown in Figure 5, wherein % transmission is plotted as a function of wavelength in nanometers (nm). Higher HCl flows (> 5 sccm for the reactor configuration used in this example) to the iron boat led to etching of gallium nitride at the baseline growth condition. Although lower HCl flows or less iron chloride would be preferred to achieve semi-insulative character, this example demonstrates that sufficient Fe can be incorporated into the GaN crystal when HCl is passed over Fe in a separate metal boat.

[00115] Example 7: General example for transition metal doping with a separate dopant boat inside the reactor.

[00116] This example demonstrates the incorporation of transition metal in the GaN crystal, using a separate dopant metal boat inside the reactor, similar to example 6.

In addition to the gallium boat, the reactor contains a separate boat for the transition metal doping. 800 grams of 99.99999% gallium are loaded into the gallium boat, and 5 grams of 99.995% metallic element chosen from Table VI are loaded into the dopant boat. A baseline growth condition is first established without dopant flow. The baseline growth conditions are: growth temperature = 1000-1050°C, growth pressure = atmospheric pressure, growth rate = 100-250 $\mu\text{m}/\text{hr}$. In a subsequent growth, the HCl flow for the dopant boat is turned on, while other conditions are identical to the baseline growth condition. The HCl flow is 1-100 sccm. The transition metal element is transported to the growth zone by HCl and carrier gas, incorporating the transition metal dopant into the growing GaN crystal.

[00117] The foregoing generalized procedure is carried out for each of the metal elements listed in Table VI below.

Table VI: Metal elements for Example 7.

Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd and Hg.

[00118] Example 8: General example using metal-organic as transition metal doping source

[00119] This example demonstrates the incorporation of transition metal in the GaN crystal material, using metal compound supplied from a bubbler outside of the reactor. One of the metal-organic compounds chosen from Table VII is used. 250-7000 grams of 99.99999% gallium are loaded into the gallium boat (reservoir) at room temperature (~25°C). The reactor is sealed and the reactor temperature is raised to the growth temperature. A baseline growth condition is first established without bubble flow. The baseline growth conditions are: growth temperature = 1000-1050°C, growth pressure = atmospheric pressure, growth rate = 100-250 $\mu\text{m}/\text{hr}$. In a subsequent growth, the bubble flow is turned on, while other conditions are identical to the baseline growth condition. The transition metal element is transported to the growth zone by the bubbler carrier gas, incorporating into the growing GaN crystal.

[00120] The foregoing generalized procedure is carried out for each of the metal-organic compounds listed in Table VII below.

[00121] Table VII

Metal-organic compounds for example 8
Bis(cyclopentadienyl)chromium
Bis(cyclopentadienyl)cobalt
Bis(cyclopentadienyl)iron
Bis(cyclopentadienyl)manganese
Bis(cyclopentadienyl)molybdenum dichloride
Bis(cyclopentadienyl)nickel
Bis(cyclopentadienyl)osmium
Bis(cyclopentadienyl)ruthenium
Bis(cyclopentadienyl)tungsten dichloride
Dimethylzinc

[00122] The foregoing examples illustrate the approach of the invention for forming large area, free-standing semi-insulating gallium nitride, and the characteristics of the large area, free-standing, semi-insulating gallium nitride that is produced by such growth techniques. Semi-insulating gallium nitride manufactured in accordance with the invention is a useful substrate material for the fabrication of electronic and/or optoelectronic GaN devices, including GaN devices that heretofore have been fabricated on heteroepitaxial substrates such as sapphire, silicon carbide, etc.

[0083] While the invention has been variously described herein with respect to specific features, aspects and embodiments, it will be appreciated that the scope of the invention is not thus limited, but rather extends to and includes such modifications, variations and other embodiments as will readily suggest themselves to those of ordinary skill in the art, based on the disclosure herein.

[0084] Accordingly, the invention is intended to be broadly construed, as encompassing all such other modifications, variations and alternative embodiments, as being within the spirit and scope of the invention as hereinafter claimed.